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Ethylene Oligomerisation Catalysts: Synthesis, Evaluation and Mechanistic Studies

by

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Statement of Co-Authorship

The following people and institutions contributed to the publication of work undertaken as part of this thesis:

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Located in chapter 2

The candidate was the first author (25 %) and contributed to designing and performing experiments detailed therein. The candidate also contributed to the final refinement of the manuscript. Author 1 (20 %) contributed to experimental design, preparation and submission of the manuscript. Author 2 (20 %) performed solid state structural analysis and contributed to the preparation of the manuscript. Author 3 (15 %) performed experiments for the manuscript. Authors 5 and 6 (5 % each) contributed to the final refinement of the manuscript.

Paper 2: Mechanism of ethylene dimerization catalyzed by $Ti(OR')_4/AlR_3$

Located in chapter 3

The candidate was the first author (60 %) and was responsible for contributing to experimental design, performing experiments and data analysis. The candidate was also responsible for preparing the manuscript (first draft). Author 1 (40 %) contributed to the experimental design and data analysis. Author 1 also finalised and submitted the manuscript for publication.

Paper 3: Ethylene polymerisation and oligomerisation with arene-substituted phenoxy-imine complexes of titanium: investigations of multi-mechanistic catalytic behaviour.

Located in chapter 4

The candidate was first author (55 %) and contributed to designing and performing experiments and preparing the first draft of the manuscript. Author 1 (20 %) contributed to experimental design and refinement and submission of the manuscript. Author 2 (20 %) collected and refined solid state data for the manuscript and contributed revisions to the final manuscript. Author 6 (5 %) contributed to the final refinement of the manuscript.

Paper 4: Synthesis of Ti(IV) complexes of donor-functionalised phenoxy-imine tridentates and their evaluation in ethylene oligomerisation and polymerisation.

Located in chapter 5

The candidate was first author (40 %) and contributed to designing and performing experiments and preparing the first draft of the manuscript. Author 3 (15 %) contributed to performing experiments detailed therein. Author 1 (20 %) contributed to experimental design and refinement and submission of the manuscript. Author 2 (20 %) collected and refined solid state data for the manuscript and contributed revisions to the final manuscript. Author 6 (5 %) contributed to the final refinement of the manuscript.

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Abstract

The oligomerisation of ethylene to linear alpha olefins is an important industrial process for the production of polyethylene co-monomers, plasticizers, surfactants and waxes. With the ever increasing market demand for short chain linear alpha olefins (1-butene, 1-hexene and 1-octene) there has been intensive research in both industry and academia on methods to selectively oligomerise ethylene to form only the short chain fractions. As such, a range of novel catalysts based on titanium and chromium have been synthesised and characterised. Their behaviour in ethylene oligomerisation and polymerisation has been studied. In most cases, the mechanism of oligomer formation has been investigated.

A range of aryloxy- and alkoxy- ligands, both monodentate and chelating, have been reacted with Ti(IV) to give complexes of the form $[Ti(OAr)_2Cl_2]$, $[Ti(O\text{^}OR)Cl_3]$ and $[Ti(O\text{^}OR)_2Cl_2]$ (R = aryl, alkyl). X-ray crystallography of selected samples has revealed that the complexes vary in the Lewis base solvation and/or aggregation state. The complexes have been evaluated as ethylene oligomerisation catalysts in conjunction with alkylaluminium activators such as triethylaluminium and methylaluminoxane. Polymerisation is the major process, however, ethylene oligomers such as dimers and higher oligomers also result. The bimodal distribution of products indicates a number of active species arise when the catalyst is activated. Deuterium labelling studies are consistent with a metallacycle mechanism for oligomer formation.

The mechanism for the catalytic dimerisation of ethylene with the industrially relevant Alphabutol-type catalysts has been explored. Catalysis with $Ti(OBu)_4/AlMe_3$ and a mixture of ethylene/perdeuteroethylene, followed by isotopomer analysis via GC-MS, has revealed the major product 1-butene and the ethylene/1-butene codimers result from a Cossee mechanism rather than the commonly reported metallacycle mechanism.

A range of unsubstituted and 6-substituted *ortho*-phenoxy-imine ligands have been prepared and converted to their silyl ether derivatives. Reaction of silyl ethers with $TiCl_4(thf)_2$ in the case of the unsubstituted species yields bis-ligated complexes while the substituted species react cleanly to yield complexes of the form [Ti(O^NR)Cl_3(thf)]. In most cases the complexes have been characterised by X-ray crystallography. Testing of the complexes for ethylene oligomerisation and polymerisation has been undertaken employing alkylaluminium co-catalysts. In all cases the predominant product formed is polyethylene. However, careful analysis of the liquid phase reveals a complex process by which 1-butene is most likely formed via a Cossee mechanism while 1-hexene results from a metallacyclic process.

A series of mono-anionic tridentate phenoxyimine (3-(*t*-butyl)-2-(OH)-C_6H_4C=N($C(CH_3)_2CH_2OMe$), 3-(adamantyl)-2-(OH)-C_6H_4C=N(2'-(2"-SMe)C_6H_4)-C_6H_4 and 3-(*t*-butyl)-2-(OSiMe3)-C_6H_4C=N($C(CH_3)_2CH_2OMe$) and phenoxy-amine (3-(adamantyl)-2-(OH)-$C_6H_4CH_2$-N(2'-(2"-OMe)C_6H_4)-C_6H_4) ligands have been prepared and reacted with $TiCl_4$ or $TiCl_4(thf)_2$ to give the mono-ligated complexes. In most cases, the solid state structure of the complexes has been determined. The complexes have been tested for ethylene oligomerisation/polymerisation in

conjunction with methylaluminoxe. They show a broad range of selectivities, which are discussed in relation to their ligand structure.

Finally, three classes of ligands have been explored for ethylene tri-/tetramerisation in conjunction with chromium and both triethylaluminium and methylaluminoxane co-catalysts. Hydrazine based ligands containing an N-H functionality [PN(NH)P], analogous to Rosenthal's previously reported PNPNH system, show selectivity towards 1-hexene and 1-octene formation in conjunction with triethylaluminium, and act as PNP tetramerisation analogues when methylaluminoxane is employed. PNP ligands containing non-protic pendant donor moieties generally show poor activity and selectivity when triethylaluminium is employed as an activator, however when methylaluminoxane is used good activities and selectivities are achieved. When oxygen is the donor atom *n*-propylcyclopentane and 2-propenylcyclopentane, and higher homologues, are produced during catalysis. The formation of such products is discussed with respect to the generation of methylenecyclopentane and methylcyclopentane by PNP based tetramerisation catalysts. Simple phosphine ligands containing O-H functionalisation are also explored and it was shown that the catalyst selectivity is highly dependent on both the activator and structural features of the ligand employed.

Table of Contents

Abbreviations

Ar	Aryl
$CDCl_3$	Deuterated chloroform
DCM	Dichloromethane
Et	Ethyl
GC	Gas chromatography
GC-MS	Gas chromatography-Mass spectrometry
GTL	Gas-to-liquid
HDPE	High density polyethylene
LAO	Linear alpha olefin
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MAO	Methylaluminoxane
Me	Methyl
MS	Mass spectrometry
NMR	Nuclear magnetic resonance
PE	Polyethylene
THF	Tetrahydrofuran
TBAF	Tertbutylammonium fluoride
TON	Turn-over number